

# Electrode Material Migration During Pulsed Electric Field (PEF) Treatment

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**Abstract**—Electrochemical reactions, especially those involving the electrode material, are considered one of the challenges facing the commercialization of the process of food preservation using pulsed electric fields. These undesired reactions lead to the migration of electrode material components into the food under treatment affecting food quality and taste, electric field distribution, and electrodes' life time. Fortunately, electric pulse parameters, reaction temperature, and electrode material can be used to control the rate of electrochemical reactions. This paper studies the effect of pulse parameters on the concentration of metals after applying electric pulses to aqueous solutions with various pH values. It is the first step in the research work targeting the optimization of electrode material migration under real food preservation process using pulsed electric fields.

## I. INTRODUCTION

The use of pulsed electric fields (PEFs) is an alternative way for liquid food preservation rather than conventional thermal pasteurization. Microbial cells which are exposed to an external electric field for few 10s of nano-seconds to a few microseconds, respond by an electrical breakdown and local structural changes of the cell membrane [1]. In consequence, a drastic increase in permeability is observed which is equivalent to a loss of viability. This is verified by the inactivation of various microbial species resulting in an extended shelf life of liquid food such as: milk, orange juice, apple juice, and beer [2]. This method has the advantage of retaining the heat-sensitive compounds originally found in the liquid food itself, and hence improving both nutrition and sensory aspects.

On the other hand, the system used for PEF treatment is a high voltage power source supplying short pulses to the food under treatment through two electrodes. This system also acts as an electrochemical cell, and as a result, some undesirable oxidation/reduction reactions might take place at the electrode/electrolyte interface leading to electrode material migration into the food under treatment. Consequently, some metal ions may be present in the treated food affecting both the quality and sensory aspects. Further, the electric field distribution may be affected, and the electrodes' life time is reduced.

This research work will investigate the effect of pulse parameters (peak voltage, polarity, and number of pulses) and solution characteristics (pH) on the electrode material migration in aqueous solutions.

## II. ELECTRODE MATERIAL MIGRATION

Electrochemical effects of PEF treatment are first mentioned by Bushnell et al. [3] where an embodiment was patented to reduce these effects. Only theoretical analysis was presented based on the time required for charging the double layer capacitor at the electrode/electrolyte interface. It was proved that by removing all the residual charge from one electrode during the discharge period, an approximately zero net charge is delivered to this electrode, thereby reducing electrochemical effects.

The first attempt to study the migration of electrode material during PEF treatment is presented by Morren et al. [4]. Based on some theoretical analysis, an equivalent circuit was derived to account for electrochemical reactions showing that at each voltage level, there is a maximum pulse width above which corrosion starts. This pulse width corresponds to the charging time for the double-layer capacitor. It was experimentally verified using a sinusoidal waveform of 15 V and 150 V peak-to-peak and a frequency range of 0.1 Hz to 10 kHz applied to stainless steel electrodes of 10 mm spacing with an aqueous solution of NaCl. Although the experimental work is far from the conditions of real PEF treatment, the observations have some relevance. Use of materials with a very high value of double-layer capacitance was suggested to increase the maximum allowable pulse width.

Ecrendilek et al. [5] carried out a comprehensive assessment of PEF processing of beer through microbial, sensory, and quality analysis. PEF treated samples were analyzed by trained sensory panelists showing a significantly lower rating against untreated samples for flavor and mouth feeling. Measuring the concentration of metals in beer samples before and after PEF treatment showed a significant increase in Fe, Cr, Zn, and Mn. It was concluded that migration of electrode material impacted the sensory attributes through only this experimental assessment of real PEF treatment. Authors suggested using more stable electrode materials to ensure minimum impact of PEF processing.

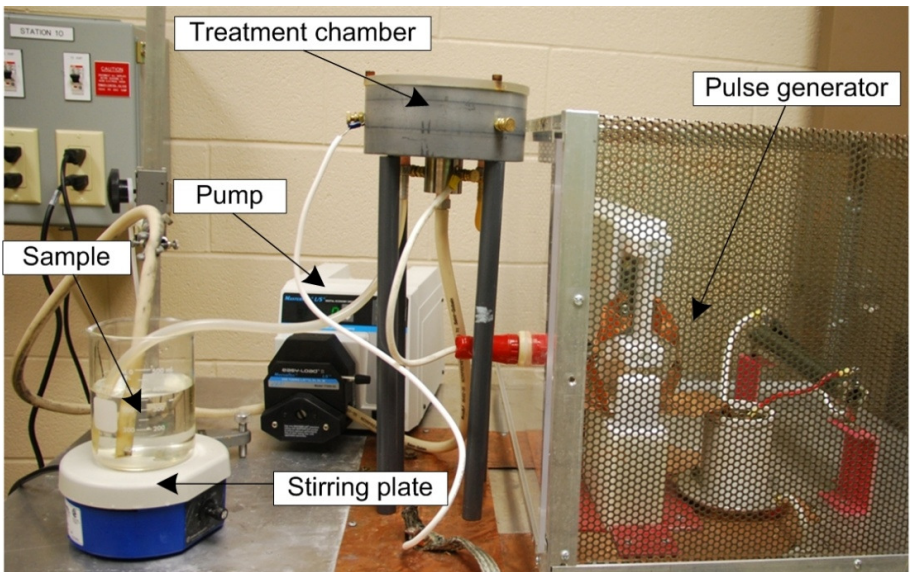


Fig. 1. The experimental setup used for the PEF treatment.

Roodenburg et al. [6,7] discussed the problem of electrode material migration in detail taking into account both theoretical analysis and experimental work. The effect of three pulse shapes on the metal concentration in aqueous solution of NaCl concluded that oscillatory pulses (featuring positive and negative voltages) are preferred than exponential pulses (featuring only positive or negative voltages). The electrode material migration, in addition to microbial inactivation was studied in orange juice samples. Repetitive PEF treatment was applied to obtain metal concentration above the limit of detection (LOD) of the measuring equipment. Some samples were circulated through the system without applying any pulses to assess the effect of the stainless tubing, and hence separating the dissolved metals into its components; tubing effect and PEF effect. Although using orange juice resulted in higher values of metal release per unit transferred charge compared to the aqueous solution used earlier, the concentration of metals was far below the maximum allowable levels in standards for fruit juice and drinking water. Using the measured values of metal concentration, the electrode life time was estimated based on the reduction of electric field below a certain threshold due to change in chamber geometry caused by the metal release from electrodes. The expected life time was very short (760 h); and by considering that the damage to the electrodes cannot be completely related to metal concentration measured since some of the dissolved metals may be deposited on the electrodes themselves, the life time will be much shorter. It was suggested to increase the peak of the voltage pulses gradually to compensate for the electric field reduction caused by the change in chamber geometry, and hence increase the number of hours in which the chamber can be used for effective PEF treatment (without reducing the rate of electrode reactions) [7].

### III. DESCRIPTION OF EXPERIMENTAL SETUP

The experimental setup used for the PEF treatment is shown in Fig. 1.

#### A. Pulse generator

Short exponential-decay pulses are generated by charging two parallel capacitors, 0.3 microfarads each, through a high voltage dc source operating in constant current mode. The capacitors are discharged through the treatment chamber using a thyatron switch. The pulse width depends on the resistance of the treatment chamber load. This pulse generator is capable of generating negative pulses with a repetition rate 1-20 pps and a peak up to 30 kV. During the experimental work presented in this paper, the pulse repetition rate is fixed at 10 pps. A schematic diagram of the pulse generator circuit is shown in Fig. 2.

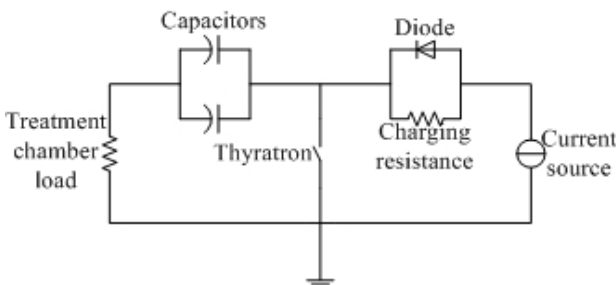


Fig. 2. A schematic diagram of the pulse generator circuit.

### B. Treatment chamber

The fluid treatment chamber comprises of housing and an electrode assembly. The housing comprises a fluid inlet for receiving the fluid to be treated and a fluid outlet for allowing treated food to be retrieved. The electrode assembly is located within the housing and has two electrodes for generating an electric field between them. The electrodes have opposing convex electrode surface sections defining there between a biconcave treatment zone for treatment of the fluid by the most intense electric field generated by the electrode assembly [8].

The electrode assembly is made of stainless steel (type 316) with a gap spacing of 2 mm. Electron Scanning Microscope (ESM) is utilized to analyze the composition of the electrode material. The main elements and their percent weights are listed in Table 1.

TABLE 1: ELECTRODE MATERIAL COMPOSITION.

Element	Weight (%)
Iron (Fe)	66.27
Chromium (Cr)	17.26
Nickel (Ni)	11.44
Molybdenum (Mo)	2.92
Manganese (Mn)	2.11

### C. Test samples

For this experimental work, samples are simple aqueous solutions prepared by adding NaCl and HCl to distilled water to adjust the electrical conductivity and the pH, respectively. Oakton® CON 110 Conductivity/TDS Meter and Oakton® Waterproof pHTestr™ 10 Pocket pH Tester are utilized during samples preparation to measure the values of electrical conductivity and pH, respectively. Table 2 shows the electrical and chemical characteristics for some liquid food commonly used when testing the effectiveness of PEF treatment. It can be seen that the electrical conductivity ranges from 1.58 to 5 mS/cm, therefore all samples are prepared with a fixed conductivity of 2 mS/cm which falls in the above mentioned range. The reason behind fixing the conductivity at a certain value is maintaining the pulse width of all generated pulses almost the same. To simulate the effect of acidity of some liquid food, samples of pH equals 3.5 are compared to others of pH equals 7.

TABLE 2: ELECTRICAL AND CHEMICAL CHARACTERISTICS OF SOME LIQUID FOOD.

Liquid food	Electrical conductivity	pH
Beer [4]	1.58 mS/cm	-
Orange juice [7]	3 mS/cm	3.8
Apple juice [9]	2 mS/cm	-
Milk [10]	2-5 mS/cm	6.7-7.0

#### IV. PROCEDURE OF EXPERIMENTAL WORK

To quantify the amount of electrode material migration so as to study how it varies with operating parameters, the concentration of metallic elements in the treated samples could be taken as an index. It can be measured using the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipment. The ICP can directly measure the concentration of metal elements in the treated samples without any acidic/heating digesting procedure due to the simple matrix of aqueous solutions. However, 10 drops of concentrated HCl is to be added to the collected samples just after treatment because it is preferred for the ICP to operate in acidic medium.

The limits of detection (LOD) of the used ICP for iron (Fe), chromium (Cr), nickel (Ni), and manganese (Mn) are 7.1, 6.1, 13.4, and 2.1  $\mu\text{g/L}$ , respectively. These limits are much above the expected concentration of metals after real PEF treatment [6,7]. Consequently, the samples are circulated in a closed loop system so that repetitive treatment is applied and metal concentration accumulates. During the experimental work presented in this paper, the flow rate is fixed at 1500 mL/min.

In the following subsections, three sets of experiments are described in detail to study the effect of number of pulses, voltage level and polarity, and solution pH on the electrode material migration. The samples for each set of experiments are prepared together to ensure identical samples and the experiments within such a set are carried out in a random order to reduce the effect of any time dependence of experiments, if exists. Tap water is circulated for at least 5 minutes through the treatment chamber after each experiment to cool the chamber down and rinse the electrodes. All experiments are performed at room temperature and no cooling/heating system is equipped. The concentration of metallic elements in the samples of each set are measured together in a single session of the ICP equipment to avoid any calibration changes as the ICP is to be calibrated in the beginning of any session.

##### *Experiment A. Effect of number of pulses*

Electric pulses of 4 kV peak are applied to samples of 1000 mL size and pH of 7. Measurements are taken after 30, 60, 90, 120, and 150 min. Because of closed loop treatment, each 30 min represents 18 pulse/mL. Each experiment was repeated 5 times.

##### *Experiment B. Effect of voltage level and polarity*

Electric pulses are applied for 30 min to samples of 400 mL size and pH of 7. The peak voltage of pulses is adjusted to 2, 4, and 6 kV. Then, the experiment is carried out with 6 kV peak after reversing the terminals of the treatment chamber, i.e. applying the negative pulses to the outer electrode. Here, each 30 min represents 45 pulse/mL. Each of these 4 experiments were repeated for 3 times.

##### *Experiment C. Effect of solution pH*

Electric pulses of 4 kV peak are applied to samples of 400 mL size. Measurements are taken after 30 and 60 min. Similar to part (B), each 30 min represents 45 pulse/ mL. Experiments were repeated 3 times with samples of pH equals 7 and 3.5, respectively.

## V. RESULTS AND DISCUSSION

IBM® SPSS® Statistics (version 19) package is used for the statistical analysis of the obtained results. Plots and bar-charts are produced for the mean values with error bars representing 90% confidence intervals. As a primary observation, obtained results suffer from a large variability and, in some cases, the variance changes significantly with the independent variable.

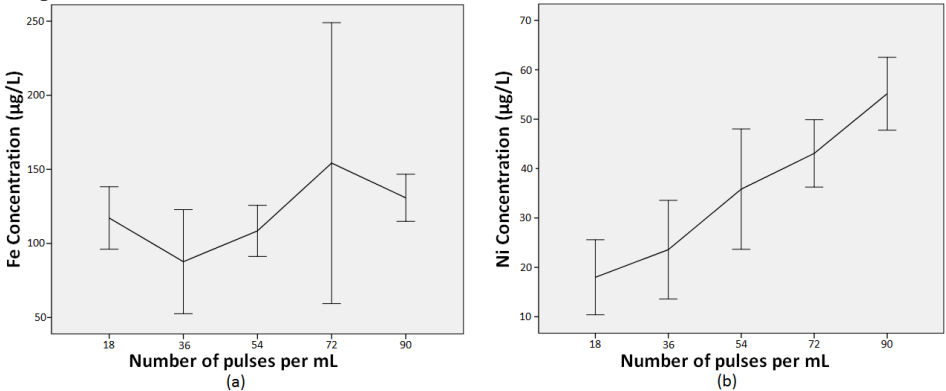


Fig. 3. Concentration of (a) iron and (b) nickel in test samples under experiment (A). Negative pulses are applied to the inner electrode.

Fig. 3a shows the concentration of iron varying with the number of pulses. It was expected that the mean concentration would increase with the number of pulses, but it is not clearly following any trend. From statistical point of view, there is no evidence suggesting that the concentration of iron varies with the number of pulses. It is also clear that the variance changes significantly from one point to another.

The ICP was also used to measure the concentration of nickel in the same samples that are used for iron. Nickel mean concentration showed an increasing trend with the number of pulses as shown in Fig. 3b. In addition, the variance is almost the same for all points. This suggests that one source of variability can be originated from the iron itself, as it could have gone into further reactions either with the solution or with the electrodes. Therefore, concentration of nickel may be preferred over that of iron as an index of the electrode material reactions.

During experiment (B), the concentration of all possible metals is measured in each sample. In this experiment, the concentration of nickel was below the LOD of the ICP for most of samples. Hence, the concentration of chromium with varying the peak of the voltage pulse is compared to that of iron as shown in Fig. 4. Both metals have almost the same trend with increasing the peak of the voltage pulse. It can be seen that the trend is far from linearity and that the variance increases gradually with the voltage level. One of the reasons behind these observations could be the effect of temperature rise which is discussed later.

In experiment (B), the effect of polarity is also studied. A significant reduction in the concentrations of iron and chromium is observed when the negative pulses are applied to the outer electrode. The reason behind this reduction is that the surface area of the outer electrode is larger than that of the inner one. Since the electrochemical reactions involving electrode material theoretically take place at the anode (oxidation processes), revers-

ing the connection of chamber terminals reduces the surface area of the anode which reduces the reaction products.

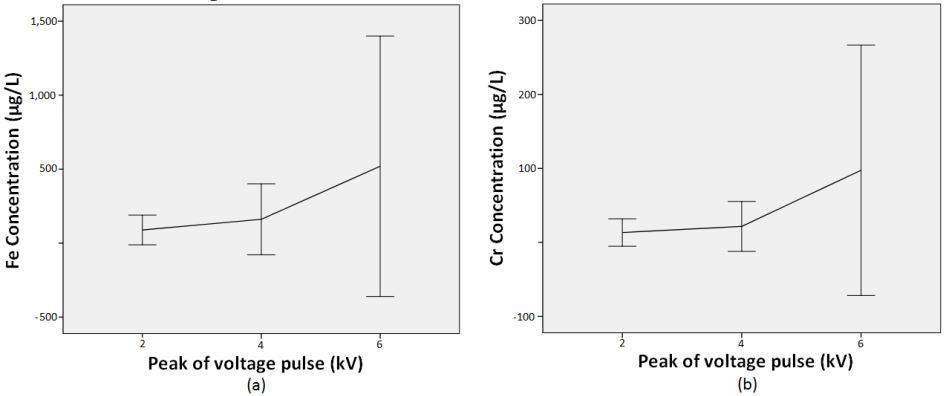


Fig. 4. Concentration of (a) iron and (b) chromium in test samples under experiment (B). Negative pulses are applied to the inner electrode.

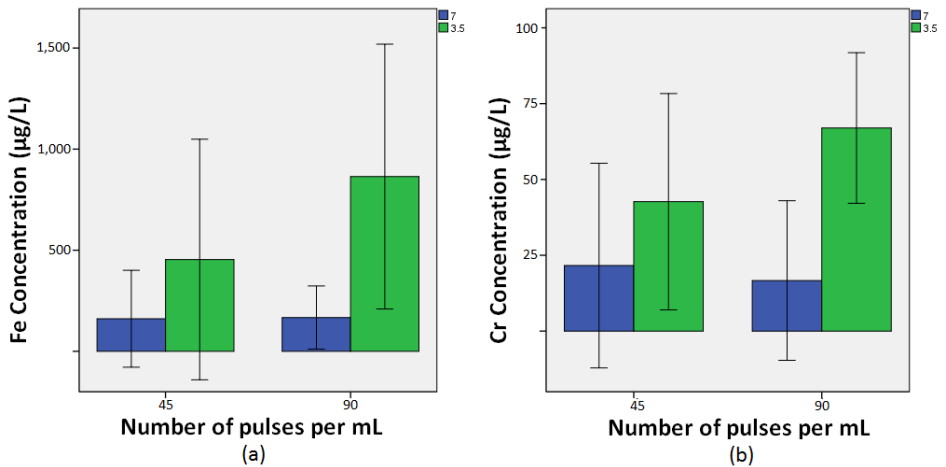


Fig. 5. Concentration of (a) iron and (b) chromium in test samples under experiment (C). Negative pulses are applied to the inner electrode.

Experiment (C) is to verify that low-pH solutions will have higher concentration of metals as shown in Fig. 5. This can be easily explained by knowing that lower pH means higher concentration of hydrogen atoms which will enhance the reduction half-cell reactions at the cathode. Consequently, oxidation half-cell reactions at the anode including electrode material migration will be enhanced. This recommends that acidic beverages such as orange juice will face higher problems with electrode material migration than non-acidic beverages of the same electrical conductivity such as beer and apple juice. The effect of type of acid requires further investigation.

Two important observations should be taken into account for any future work. An increase of sample temperature is observed during the experiments, especially when the experiments last for 150 min at 4 kV or when they last for 30 min at 6 kV. The sample

temperature reached  $55^{\circ}\text{C}$  in both cases, which means that the temperature inside the chamber is much higher. This temperature rise will affect the reactions in two ways; directly as the electrochemical reactions are similar to any chemical reactions where kinetics is enhanced with temperature. An indirect way in which the temperature rise causes an increase in the electrical conductivity of the samples. This was observed clearly by a gradual increase in the peak of the current pulse during the experiment (A) as shown in Fig. 6. The pulse width is also affected since the time constant of the discharge circuit depends on the resistance of the chamber load; hence, the rate of the electrochemical reactions. This temperature effect should be eliminated by controlling the temperature of samples through a cooling bath.

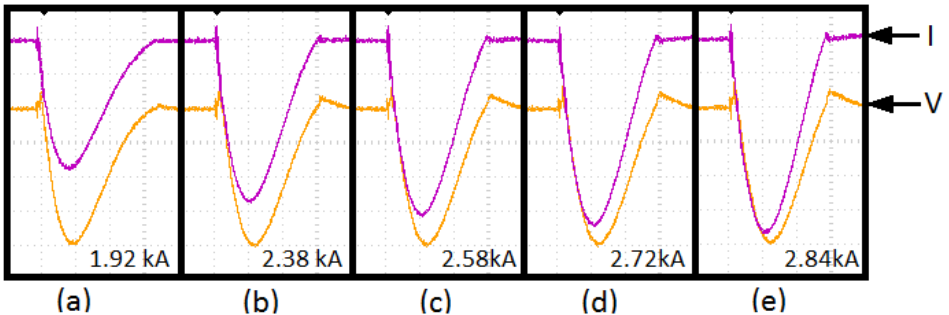


Fig. 6. Variation in the measured peak current as a function of time, with 30 min interval, for a 4 kV peak voltage pulse. Horizontal scale:  $1 \mu\text{s}/\text{div}$ ; vertical scale:  $1 \text{ kV}/\text{div}$  for voltage and  $0.5 \text{ kA}/\text{div}$  for current.

The highest concentration of iron of  $864.13 \mu\text{g}/\text{L}$  is obtained in experiment (C) when electric pulses of 4 kV peak are applied for 60 min with samples of pH equals 3.5. During this period, the sample is circulated through the chamber for 225 times to increase the concentration of metals above the LOD as mentioned earlier. If linearity with number of pulses is assumed, each pulse contributes by  $0.0096 \mu\text{g}$ . This should be multiplied by the number of pulses per unit volume to be applied during the real PEF treatment in order to find the expected metal concentration. Referring to the health-based and aesthetic guidelines for chemical/physical parameters of drinking water [11], the concentration of iron should be less than  $300 \mu\text{g}/\text{L}$ .

The term real PEF treatment here means the number of electric pulses required for effective inactivation of microorganisms. However, a large differences in real PEF conditions exists in literature. The number of pulses per unit volume is calculated from [5] to be  $3,600 \text{ pulse}/\text{mL}$  and it is given in [7] as  $6.7 \text{ pulse}/\text{mL}$ . If we calculate the expected concentration of metals considering these conditions of pulses per unit volume, it will result in  $34,560 \mu\text{g}/\text{L}$  (far above the limits) and  $64.32 \mu\text{g}/\text{L}$  (far below the limits), respectively. The reason behind this difference in PEF treatments may originate from the type of microorganisms and the test conditions used.

## VI. CONCLUSIONS

This paper is the first step in the research work targeting the optimization of electrode material migration under food preservation process using pulsed electric fields. The effect of pulse parameters on the concentration of metals is studied after applying electric



pulses to aqueous solutions with various pH values. Although the concentration of dissolved metals in the treated samples does not represent the actual rate of electrode reactions due to the deposition of dissolved metals on the electrode surface, it can be used as an index to show how electrode reactions vary with various parameters. This deposition also resulted in higher variability when observing iron rather than other elements of the stainless steel alloy. It was concluded that low-pH solutions will result in higher concentration of metals and that connecting the negative terminal of the pulse generator to the electrode with larger surface area will reduce the concentration of metals.

For future work, similar experiments are to be carried out with real food to obtain the relationships of metal concentration with the number of pulses under various voltage levels. Then, these relationships can be used in conjunction with the inactivation curves from literature to optimize the pulse parameters. Besides comparing the concentration of metals at these pulse parameters with regulations for food industry, the effect of deposited metals which appears on the electrodes after operating for several hours should be studied. Further investigation may suggest the use of electrode materials featuring higher resistance to electrochemical reactions such as titanium and platinized-titanium.

## VII. ACKNOWLEDGEMENTS

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